MoS₂ nanospheres were formed using a template free hydrothermal process, which exhibit high catalytic activity towards hydrogen evolution reaction (HER). The extend of defect sites are probed by extended X-ray absorption fine structure which found decrease in co-ordination number at Mo site rather than at S site. DFT calculations identified an uneven strain and defect distribution between two S planes of curved MoS₂. Based on hydrogen adsorption on various sites, we identify a new pathway called "extended activity @ shielded defects", for Volmer-Tafel and Volmer-Heyrovsky mechanisms, where H adsorption occurs at exposed S layer driven by defects in underneath S layer of nanosphere. Having higher defect concentration it exhibited excellent HER activity with over-potential of −0.12 V, Tafel slope of 90 mV/decade, and higher turnover frequency. Our findings provide an avenue to design and engineer advanced nanostructures for catalysis, electronic devices, and other potential applications.

Introduction

 Hydrogen generation through water electrolysis has been extensively investigated as an attractive way to produce fuel from renewable source. The most effective electrocatalytic materials for hydrogen evolution reaction (HER) are Pt group metals, but their high cost and scarcity limits their widespread use. As such, developing efficient and inexpensive HER catalyst with comparable activity and stability is highly desirable but remains challenging. So far, both theoretical and experimental studies have highlighted the great promise of layered transitional-metal dichalcogenides, such as molybdenum disulphide (MoS₂) and its derivatives, as efficient and low cost catalysts for HER.

In the hexagonal crystal structure, 2H-MoS₂ monolayer is direct band gap semiconductor of band gap 1.8 eV due to which the electrocatalytic activity cannot be expected in its pristine form. But unsurprisingly its peripheral edges and basal plane defect sites are two different origins of catalytic activity, as confirmed by both experimental and theoretical studies.

According to many reports which are focusing on edge effects, the unsaturated sulphur atoms on the edges play a crucial role in HER catalysis and so increasing number of such sulphur atoms was proposed to be an efficient pathway to enhance the HER activity. Whereas the S point defects on the basal plane catalyse differently by availing the Mo atom for reduction of H⁺. These two different active sites have different electronic conductivity that is another crucial factor of performance of the electrocatalyst. Even though the bulk portion is semiconducting in nature, the peripheral edges have metallic character due to the edge states whilst the defects on the basal plane create mid-gap states which decrease the band gap. In this regard, a metallic phase (1T phase) of MoS₂ was much attracted because of its good activity over its semiconducting phase. Although it has been proved as an exciting HER catalyst, its activity is limited by its poor stability. But co-existence of these two (2H and 1T) phases are found to have better stability and activity and supercapacitive behaviour. Even though 1T phase is electronically suitable, the 2H phase with engineered defects or edges outperforms with good stability. As a result, tremendous efforts have been made to...
engineer the accessible edge structure of 2H-MoS$_2$ catalysts for exposing active sites. It is worth to mention here that few recent attempts have been made to uncover the role played by the defects sites in electrocatalysis. For example, Dou et. al., demonstrated that NH$_3$-plasma treatment leads simultaneous N-doping in Co$_3$S$_8$ and etching of underlying graphene support which results a significant enhancement in bi-functional activity of Co$_3$S$_8$/graphene material towards oxygen electrode.$^{[12]}$ Similarly, Xu et. al., identified the generation of highly active oxygen vacancies on Ar plasma treated Co$_3$O$_4$ material which resulted enhanced OER activity.$^{[13]}$ Very recently, Liu et. al., successfully realized the in situ exfoliation of edge/defect-rich and oxygen-doped graphene on the surface of carbon fibers, by treating carbon cloth with Ar plasma.$^{[14]}$ The resulting material becomes a self-standing electrocatalyst for both OER and ORR with an exceptional activity.

Recently, Bard and his group$^{[15]}$ have used substrate directed growth using CVD techniques for the formation of curved MoS$_2$ surface with strain which is an efficient way to populate the S defects and therefore to increases the activity of the catalyst. To achieve this, they have deposited MoS$_2$ on gold spheres which mould the curvature of MoS$_2$ surface. In another way, the Norskov and his group$^{[16]}$ used plasma assisted post processing techniques to achieve in-plane strain in basal plane of MoS$_2$. These two studies guided us to search a simple way to achieve similarly strained MoS$_2$ surface. Ultimately the formation of nanospheres is our obvious choice using a simple hydrothermal method$^{[16]}$ where all these chemicals are toxic. Moreover, this work compares the activity of MoS$_2$ nanosheets, nanoflakes with that of nanospheres. These different morphologies are obtained for different Mo precursor along with sulphur source during hydrothermal process as described in supporting information. In order to uncover the facts behind morphology and coordination number of Mo and S atoms in aforesaid catalysts, TEM and HAADF-STEM microscopic technique and XAFS technique were employed, respectively. Since the defects identified in XAFS are electrochemically ambiguous, linear sweep voltammetry (LSV) is carried out to confirm electrochemically accessible active sites which is also found to be higher in nanospheres.

**Morphological Analysis**

To begin with, the synthesized electrocatalysts whose FE-SEM, TEM and HAADF-STEM micrographs are shown in Figure 1 have been characterized by X-ray diffraction to confirm the formation of 2H-MoS$_2$. Occurrence of high intensity peaks including (002) in all the samples shows the formation of a crystalline 2H-MoS$_2$ with a well-stacked layered structure (refer supporting information, Figure S1). Figure 1 indicates each sample possess intrinsic morphology depending on experimental conditions. FE-SEM image of nanosheets display range in micrometer whereas TEM images of nanospheres and nanoflakes in nanometer region. The nanospheres are approximately 10 to 100 nm in diameter, in addition, there are small and damaged spheres on the walls of larger ones. Unlike nanosheets which are observed as well stacked bundles, the nanoflakes display crumpled sheets of MoS$_2$ with few hundred nanometer in dimension. Overall, the nanospheres are smaller in dimension on comparing sheets and flakes which in turn resulted in larger
BET surface area (refer supporting information, Table S1). Furthermore, the high angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and Energy-dispersive X-ray spectroscopy (EDS) mapping analysis are employed to probe hollow nature of the nanosphere. Figures 1D, E and F corresponding to the HAADF-STEM image and its EDS mapping depth profile for Mo and S. The latter show that the elements are seen selectively abundant on walls but not in the interior.

**Nature of Mo and S Site Environments**

The chemical states of samples were characterized by X-ray absorption fine structure (XAFS) measurements which are shown in Figure 2 A along with that of MoS$_2$ standard. Figure 2B shows $k^3$- weighted $\chi(k)$ XAFS spectra of Mo K-edge for MoS$_2$ nanomaterials. The k-range of 2.0- 10 Å$^{-1}$ has been used for Fourier transform (FT) of Mo EXAFS data. Figure 2C-F show the FT of $k^3$-weighted of Mo K-edge for MoS$_2$ nanospheres. As shown in Table S2, the coordination numbers of Mo–Mo and Mo–S are significantly less in all the four samples compared to the bulk values. Especially, the coordination numbers of Mo and S are lowest for the nanospheres. Chung et al. defined a term called the ratio of the coordination (Ns/NMo) of Mo–S and Mo–Mo to quantify the number of sulphur edge sites, lesser the ratio more the sulphur edge sites. In the present case the sulphur edge sites increase in the order of MoS$_2$ bulk &$\lambda$r; nanosphere &$\lambda$r; nanosheet &$\lambda$r; nanoflake cases. Exposing an edge site on sphere geometry is unlikely and in contrary in flakes contain more edges.

**Atomic Insights from DFT Calculations**

Morphological and defect population studies conclude that nanospheres possess more under coordinated Mo atoms, which are very essential for betterment of catalyst. To uncover atomic level insights, DFT calculations are employed on planar and curved MoS$_2$ sheets and the optimized structures are depicted in Figure S5 (Supporting Information). Also in Figure 3B a typical curved MoS$_2$ layer can be seen. It shows that the curved sheet is periodically crumpled with radius of curvature (R) of 1.33 nm for Mo layers. So the R value of top and bottom sulphur planes will be R + 1.158 Å and R - 1.158 Å, respectively. As the result of increasing the strain on sheet, the ground state energy is also increased as expected. Howbeit such curvatures are formed due to the synthetic conditions and nature of precursors used in our experiments. The calculated values of average Mo–Mo bond distance in flat and curved sheets are 3.14 Å and 3.02 Å, respectively. This decrease in Mo–Mo distance is in corroboration with XAFS measurements. On the other hand, the S–S distance is increased for S1 region and is decreased for S2 region. As the consequence, there will be more strain in S2 region owing to Columbic repulsion between the S atoms. Since the development of strain is
different on S1 and S2 region, the defect formation energy per S atom \( E_D \) will vary significantly. Thus, the \( E_D \) is separately calculated to be 2.70 eV and 0.60 eV, respectively for S1 and S2 sites, using the formula given in supporting information. From this, it is obvious that \( E_D \) is smaller for S2 site. Consequently, the inner S sphere of MoS\(_2\) nanosphere would be more viable for population of S defects due to increased strain and lower \( E_D \). To support this, we have done a simple calculations as elaborated in supporting information.

**Chemical States of Elements**

Aforesaid experimental and theoretical results are on par to evidence that the S defects are more feasibly formed on the curved surfaces of a MoS\(_2\). The creation of significantly more defects can result in changes in oxidation state of Mo and chemical composition of nanospheres. So the X-ray photoelectron spectrum was recorded for all three catalysts. As shown in top panel of Figure 4, in all the three samples the common peaks arising from Mo 3d\(_{5/2}\) and Mo 3d\(_{3/2}\) states located at 229.1 and 232.1 eV, suggesting the dominant oxidation state present in the samples is Mo\(^{4+}\).\(^{[6b]}\) It proves that the hydrothermal reduction process have been effectively carried out as explained in supporting information. Similarly for S\(^{2-}\), 2p\(_{3/2}\) and 2p\(_{1/2}\) are observed at 162.0 eV and 163.0 eV, respectively.\(^{[6b]}\) It is important to note that peaks for disulphide (S\(_2^2-\)) or polysulfide ions are not observed in our samples. Mainly such polysulfide ions will present only on the edges rather than basal planes; so this again proves that the edge to basal plane ratio is very less in the prepared samples.

**Electrocatalysis and Activity Evaluation**

In Figure 4, among the MoS\(_2\) catalysts, the nanosphere catalyst possess superior activity supported by much lower onset potential at 120 mV on comparing that of nanosheets and nanoflakes. In addition, nanosphere exhibits significantly large current density with Tafel slope of 90 mV/decade when compared 110 and 180 mV/decade. Under given conditions, when the Volmer reaction is the rate-limiting step of HER, a slope of 120 mV/decade is observed, whereas if Heyrovsky or Tafel reactions act as the rate-limiting step, Tafel slopes of 30 and 40 mV/decade can be obtained, respectively.\(^{[4a, 20]}\) For a complete HER process, combinations of these two steps should be involved to produce H\(_2\). Although the HER mechanism for MoS\(_2\) nanospheres still remains inconclusive due to the reaction complexity, the Tafel slope values are indeed very close to the value of 140 mV/decade reported for a CVD grown single layer MoS\(_2\) coated on glassy carbon\(^{[21]}\) (see support information).

Besides the HER activity, stability is another significant criterion to evaluate an advanced electrocatalyst. Long-term cycling stability of nanosphere MoS\(_2\) is investigated by performing continuous cyclic voltammetry (CV) between −0.3 and
0.1 V [RHE] at 50 mV s⁻¹. A negligible difference was observed between the LSV curves measured at the initial cycle and after 1000 cycles of CV operation, suggesting the excellent durability of nanosphere MoS₂ catalyst during long-term cycling. Note that our recent work displayed a significant activity and stability over 200 hours of operation for MoS₂ nanosphere catalyst in a single cell water electrolyzer unit. [22]

Site Dependent H Adsorption/Desorption Energy Trade-Off

The above electrochemical measurements provide enough support that the nanospheres have highest activity and good stability to be employed in real devices. Also, the reduced activity in nanoflakes and nanosheets is explained by population of less number of active sites confirmed from XAFS. So our interest lies on revealing the surface chemistry behind the activity originated from edges and exposed and concealed point defect sites in nanosphere catalyst. The optimized structure of H and H₂ adsorbed curved MoS₂ sheets are shown in Figure 3 and the calculated adsorption energy of H (ΔₐₜₜH) and desorption energy of H₂ (ΔₐₜₜH₂) for different sites are provided in Supporting Information. Also, the optimized structures of H/H₂ adsorbed planer MoS₂ sheets and nanoribbons are also shown in supporting information. In the case of flat sheet, the calculated values of ΔₐₜₜH are 0.62 eV and 2.43 eV on pristine surface and S1 defect sites, respectively. The small ΔₐₜₜH value of pristine sheet is due to weak interaction between fully saturated S atom and the H atom while the high ΔₐₜₜH of defect sites are resulted from strong interaction between exposed under-coordinated Mo atom and the H atom. The S–H and Mo–H bond distance respectively in the former and latter cases are 1.41 Å and 2.03 Å. In the case of curved sheet, the ΔₐₜₜH for S1 and S2-Opp sites are 2.51 and 1.27 eV, respectively. The S–H and Mo–H bond distance are also found to be 1.38 Å and 2.05 Å, respectively for S1 and S2-Opp sites. In order to understand the activity arising from edge S(2c) and Mo(5c) atoms, we have modelled MoS₂ ribbons as shown in Supporting Information. Similar to the point defects, the ΔₐₜₜH at Mo(5c) site is 2.45 eV which is large on comparing 1.57 eV of edge S(2c) site. All these results confirm that the ΔₐₜₜH over Mo exposed site is very high on comparing an under-coordinated S site. However, for a good HER catalyst the ΔₐₜₜH should be large and ΔₐₜₜH₂ should be small to make the site available for the subsequent reactions. So, ΔₐₜₜH₂ is also calculated and the values are reported in Supporting Information. To clearly understand the net energy trade-off in adsorption of H and desorption H₂, we have plotted the ΔₐₜₜH and ΔₐₜₜH₂ values against experimental current densities (j₀) of different catalysts, as shown in Figure 5. From this plot, it is obvious that the ΔₐₜₜH₂ for Mo exposed site is very large because two H atoms are unable to combine to yield H₂ on this site, rather it is strongly adsorbed as reduced H. So the Mo exposed active site will reduce the TOF of the catalyst. While the under-coordinated edge S atoms weakly adsorb the H which will decrease the reducing capacity of the catalyst. On comparing these, the S sites above a concealed defect site (or S2-Opp) adsorb the H strongly as well as the formed H₂ can be easily desorbed. Therefore, the concealed defect sites are expected to have optimum interactions with H and H₂ that resulted in higher activity, on comparing exposed edges and defects in planer sheets. It is worth to mention here that such (S2-Opp sites) strain induced concealed defects are only possible in the sphere morphology rather than nanosheets and nanoflakes. The long cycle life of nanosphere catalyst is due to impossible poisoning of concealed defect sites, which is uniquely observed in this case.

Conclusions

In summary, we have synthesized an efficient MoS₂ nanosphere catalyst by controlled hydrothermal reaction. The nanosphere morphology has been confirmed by FE-SEM, TEM and HAADF-STEM analysis. The significant enhancement of catalytic activity of nanospheres when compared with other two nanoshapes...
prepared in this work is attributed to strain induced concealed S defect site population uniquely plausible in sphere morphology as suggested by DFT calculations. Moreover, the calculated adsorption/desorption energy of H/H₂ supports that the concealed defects optimally interact with H and H₂ that resulted in higher activity, on comparing exposed edges and defects in planer sheets. The improved performance of nanosphere catalyst towards HER is evidenced by the lower over-potential of ~120 mV and a moderate Tafel slope when compared with other MoS₂ nanoshapes studied in this work. The construction of structure-sensitive nanomaterials with enhanced HER activity provide a feasible way to design and engineer advanced nanostructures for catalysis, nanoelectronics, photovoltaics and other potential applications.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Concealed defects · curved surface · HER activity · MoS₂ nanospheres · point defects


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